

TITLE OF THE INVENTION

A SILICON GERMANIUM SURFACE LAYER FOR HIGH-K DIELECTRIC
INTEGRATION

FIELD OF THE INVENTION

[0001] The present invention relates to semiconductor structures and semiconductor processing, and more particularly, to the use of a silicon germanium layer for integrating a high-k dielectric layer into a semiconductor device.

BACKGROUND OF THE INVENTION

[0002] In the semiconductor industry, the minimum feature sizes of microelectronic devices are approaching the deep sub-micron regime to meet the demand for faster, lower power microprocessors and digital circuits. The downscaling of CMOS devices imposes scaling constraints on the gate dielectric material. The thickness of the standard SiO₂ gate dielectric oxide is approaching a level (~10 angstroms (Å)) at which tunneling currents may significantly impact transistor performance. To increase device reliability and reduce electron leakage from the gate electrode to the transistor channel, semiconductor transistor technology is using high-k gate dielectric materials that allow increased physical thickness of the gate dielectric layer while maintaining an equivalent gate oxide thickness (EOT) of less than about 10 Å. The variable "k" refers to the dielectric constant of a material.

[0003] Integration of high-k materials into semiconductor microstructures can result in formation of an interfacial oxide (SiO₂) layer due to oxidation of the Si substrate. The presence of an oxide interfacial layer lowers the overall dielectric constant of the microstructure, thereby reducing the advantage of using a high-k dielectric material instead of SiO₂. To reduce the effect of an oxide interfacial layer on the overall dielectric constant of the microstructure, the oxide layer may need to be thin. Deposition of a high-k dielectric layer onto a Si substrate can result in uncontrolled growth of an oxide interfacial layer that is too thick for current semiconductor transistor technology.

SUMMARY OF THE INVENTION

[0004] The present invention provides a semiconductor device having a SiGe surface layer that reduces or solves the above described and/or other problems with prior art semiconductor devices.

[0005] The present invention further provides a semiconductor device having a SiGe surface layer that reduces oxidation of the substrate.

[0006] To this end, a method is provided for forming a semiconductor device with a SiGe surface layer to reduce oxidation of the substrate associated with subsequent integration of a high-k dielectric layer in the device. An oxide layer is formed between an unreacted portion of the SiGe surface layer and the high-k dielectric layer. The oxide layer may form during deposition of the high-k dielectric layer or during an annealing process carried out after the dielectric layer is formed. Alternatively, the oxide layer may form during both the dielectric formation and subsequent annealing.

[0007] In an exemplary embodiment of the invention, a method is provided for forming a semiconductor device by providing a substrate, forming a SiGe surface layer on the substrate, depositing a high-k dielectric layer on the SiGe surface layer, forming an oxide layer between the high-k dielectric layer and an unreacted portion of the SiGe surface layer, the oxide layer being formed during one or both of deposition of the high-k dielectric layer and an annealing process after deposition of the high-k dielectric layer, and forming an electrode layer on the high-k dielectric layer.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] In the accompanying drawings:

[0009] FIGS. 1A-1E represent cross-sections of structures that may be formed when carrying out an embodiment of the present invention;

[0010] FIG. 2 shows a flow diagram for forming a microstructure containing a SiGe surface layer according to an embodiment of the invention;

[0011] FIG. 3 shows a simplified block diagram of a batch-type processing system for forming a SiGe surface layer according to an embodiment of the invention;

[0012] FIG. 4 shows a simplified block diagram of another batch-type processing system for forming a SiGe surface layer according to an embodiment of the invention; and

[0013] FIG. 5 shows a simplified block diagram of a processing tool for forming a semiconductor device according to an embodiment of the invention.

DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

[0014] A method for making a semiconductor device is described. In an embodiment of the invention, a substrate is provided and a SiGe surface layer is formed on the substrate. A high-k dielectric layer is deposited on the SiGe surface layer, and an oxide layer, located between the high-k dielectric layer and an unreacted portion of the SiGe surface layer, is formed during the deposition of the high-k dielectric layer and/or in an annealing process after deposition of the high-k dielectric layer, and then an electrode layer is formed on the high-k dielectric layer.

[0015] FIGS. 1A-1E represent cross-sections of structures that may be formed when carrying out an embodiment of the present invention. In the embodiment illustrated in FIGS. 1A-1E, a substrate 150 is provided. The substrate 150 can, for example, be a Si substrate that is single-crystal Si or polycrystalline-Si (poly-Si). The Si substrate 150 can include numerous active devices and/or isolation regions. The Si substrate 150 can be n- or p-type, depending on the type of device being formed, and can, for example, include any diameter substrate, such as a substrate with a diameter greater than about 195 mm, e.g., a 200 mm substrate, a 300 mm substrate, or an even larger substrate.

[0016] As mentioned in the Background of the Invention section above, integration of high-k dielectric materials onto Si substrates can cause uncontrolled growth of a SiO₂ interfacial layer that renders the interfacial layer too thick to be compatible with the desired performance of the semiconductor device. In the present invention, a SiGe surface layer 160 is formed by depositing a SiGe material onto the substrate 150, as shown in FIG. 1B, or by alloying Ge with a surface portion of a Si substrate. The SiGe surface layer allows for direct deposition of a high-k dielectric layer onto the SiGe surface layer without using a base oxide layer at the substrate – SiGe interface, and

provides a dielectric layer with an overall low equivalent gate oxide thickness (EOT). Oxidation of the SiGe surface layer 160 prevents oxidation of the Si substrate 150 during deposition of the high-k dielectric layer 180 onto the SiGe surface layer 160 and/or during an annealing process after deposition of the high-k dielectric layer 180 onto the SiGe surface layer 160.

[0017] In one embodiment of the invention, the SiGe surface layer 160 can have a substantially uniform composition with a Ge content of about 10 atomic percent (at.%), or less. In another embodiment of the invention, the SiGe surface layer 160 can contain a plurality of SiGe sublayers each with Ge content of about 10at.%, or less. In yet another embodiment of the invention, the SiGe surface layer 160 can have a graded composition, for example where the Ge content varies from low (~0at.%) near the interface with the Si substrate 150, to high (~20at.%) near the interface with the high-k dielectric layer 170. For many applications, the SiGe surface layer may be less than about 1000 angstroms thick, preferably between about 10 angstroms and about 300 angstroms.

[0018] As depicted in FIG. 1C, a high-k dielectric layer 180 is formed on SiGe surface layer 160. High-k dielectric layer 180 contains a material featuring a dielectric constant (k) greater than that of SiO₂ (k~3.9). In addition, high-k dielectric materials may refer to high dielectric constant materials (e.g., HfO₂, ZrO₂) that are deposited onto substrates rather than grown on the surface of the substrate (e.g., SiO₂, SiO_xN_y). High-k materials may incorporate metal silicates or metal oxides such as HfO₂ (k~25), HfSiO_x, ZrO₂ (k~25), ZrSiO_x, TiO₂, Ta₂O₅ (k~26), and Al₂O₃ (k~9). In addition, high-k materials may also include nitrides such as silicon nitride (SiN).

[0019] After the high-k dielectric layer 180 is deposited, the structure shown in FIG. 1C is annealed to obtain the required structural and electrical properties. The annealing process forms an oxide layer 170 from oxidation of the surface portion of the SiGe surface layer 160 that is in contact with the high-k dielectric layer 180. As a result, the oxide layer 170 is formed between the high-k dielectric layer 180 and the unreacted portion of the SiGe surface layer 160. Alternatively, the oxide layer 170 can be formed during deposition of the high-k dielectric layer onto the SiGe surface layer or during both the deposition process and the annealing process. The presence of a SiGe

surface layer 160 between the substrate 150 and the high-k dielectric layer 180 can prevent oxidation of the substrate 150.

[0020] Next, a gate electrode layer 190 can be formed on the high-k dielectric layer 180. In addition to the traditional doped poly-Si, the electrode layer 190 can, for example, comprise at least one of W, Al, TaN, TaSiN, HfN, HfSiN, TiN, TiSiN, Re, Ru, and SiGe. Deposition of the electrode layer, deposition of the high-k dielectric layer, and annealing of the substrate, as well as etch processes generally required to complete the semiconductor device (e.g., etching of the high-k dielectric layer and the electrode layer), may be carried out by methods well known to those skilled in the art.

[0021] FIG. 2 shows a flow diagram for forming a semiconductor device containing a SiGe surface layer according to an embodiment of the invention. The process 200 starts at 210. At 220, a substrate is provided. In one embodiment of the invention, the Si substrate can contain a clean Si substrate where an oxide layer (native or chemical oxide layer) has been removed. An oxide layer can, for example, be removed from the substrate by placing it in a liquid bath containing dilute hydrofluoric acid (HF) or, alternatively, exposing it to HF gas phase etching. The dilute HF liquid solution can be a H₂O:HF (e.g., 50:1) mixture. In another embodiment of the invention, the substrate may contain an initial oxide layer. At 230, a SiGe surface layer is formed by depositing a SiGe layer onto the substrate or by alloying a surface portion of a Si substrate with Ge. The SiGe surface layer can contain oxygen if the SiGe surface layer is formed on a substrate containing an initial oxide layer.

[0022] In one embodiment of the invention, a SiGe surface layer can be formed using a Ge-containing gas and a Si-containing gas in a CVD process. The Ge-containing gas can, for example, contain at least one of GeH₄ and GeCl₄, and the Si-containing gas can, for example, contain at least one of SiH₄, Si₂H₆, and SiH₂Cl₂. The SiGe surface layer can, for example, be deposited at a chamber pressure of less than 5Torr and a substrate temperature between about 400°C and about 700°C. Deposition parameters that can be utilized to achieve the desired SiGe composition and thickness include chamber pressure, relative flows of the Ge-containing gas and the Si-containing gas, and substrate temperature. In an atomic layer deposition (ALD) process, the substrate is alternately exposed to a Ge-containing gas

and a Si-containing gas, until a SiGe surface layer with a desired thickness is formed.

[0023] In another embodiment of the invention, SiGe can be sputtered from a SiGe sputtering target onto the substrate. Subsequently, the substrate containing the sputtered SiGe layer can be annealed to form a SiGe surface layer with desired properties. In still another embodiment of the invention, a SiGe surface layer can be formed by sputtering Ge from a Ge sputtering target onto a Si substrate, and annealing the substrate to diffuse the sputtered Ge layer into a surface portion of the Si substrate. In yet another embodiment of the invention, a SiGe surface layer can be formed by exposing a Si substrate to a Ge-containing gas, and annealing the structure during and/or after the exposing.

[0024] At 240, following formation of a SiGe surface layer, a high-k dielectric layer is deposited onto the SiGe surface layer. The high-k dielectric layer may be formed using a variety of well known deposition methods, such as thermal chemical vapor deposition (TCVD), plasma-enhanced chemical vapor deposition (PECVD), atomic layer chemical vapor deposition (ALCVD), plasma-enhanced atomic layer deposition (PEALD), or physical vapor deposition (PVD), also known as sputtering. For many semiconductor devices, the high-k dielectric layer 180 may be less than about 100 angstroms thick, and more preferably between about 5 angstroms and about 50 angstroms thick.

[0025] When depositing high-k materials such as metal silicates or metal oxides using CVD, a process gas comprising a metal-containing precursor can be introduced into a process chamber containing a heated substrate. The substrate is exposed to the process gas for a time period that results in the desired deposition of the high-k dielectric layer. The process gas can further include a carrier gas (e.g., an inert gas) and/or an oxidizing gas. The inert gas can include at least one of Ar, He, Ne, Kr, Xe, and N₂. The addition of inert gas can, for example, dilute the process gas or adjust the process gas partial pressure(s). The oxidizing gas can, for example, contain an oxygen-containing gas comprising at least one of O₂, O₃, H₂O, H₂O₂, NO, NO₂, and N₂O. The role of the oxygen-containing gas in the deposition process can be to fill any oxygen vacancies in the high-k dielectric layer, or to chemically

modify the metal-containing precursor. The modification can involve interaction of the oxygen-containing gas with the metal oxide precursor in the gas phase or on the deposition surface.

[0026] During processing of the substrate, an oxide layer is formed between the high-k dielectric layer and an unreacted portion of the SiGe surface layer. The oxide layer can be formed during deposition of the high-k dielectric layer at 240, or during an annealing process at 250, or during both. The annealing process can be carried out using a process gas containing an inert gas, or alternatively, the process gas can further contain an oxygen-containing gas including at least one of O₂, O₃, H₂O, H₂O₂, NO, NO₂, N₂O. The oxide layer can be formed during the deposition at 240 by oxygen diffusion from the high-k dielectric layer to the underlying SiGe surface layer, such as where the dielectric layer is a metal oxide, or from oxidation of the SiGe surface layer by exposure to an oxygen-containing gas under oxidizing conditions.

Analogously, the oxide layer may be formed during the annealing process at 250 by oxygen diffusion from the high-k dielectric layer to the SiGe surface layer or from oxidation of the SiGe surface layer by exposure to an oxygen-containing gas under oxidizing conditions. Oxidation of the SiGe surface layer can predominantly form SiO₂ rather than GeO₂, due to the large difference in the heats of formation of SiO₂ and GeO₂. As a consequence, the oxide layer can preferentially contain SiO₂ and Ge diffusion away from the oxide can form a Ge-rich region at the oxide - SiGe surface layer interface. The annealing process at 250 can furthermore homogenize the Ge distribution in the SiGe surface layer and form a SiO₂/SiGe interface with good structural and electrical properties.

[0027] FIG. 3 shows a simplified block diagram of a batch-type processing system for forming a SiGe surface layer on a substrate according to an embodiment of the invention. The batch-type processing system 100 includes a process chamber 102, a gas injection system 104, a heater 122, a vacuum pumping system 106, a process monitoring system 108, and a controller 124. Multiple substrates 110 can be loaded into the process chamber 102 and processed using substrate holder 112. Furthermore, the process chamber 102 comprises an outer section 114 and an inner section 116. In one embodiment of the invention, the inner section 116 can be a process tube.

[0028] The gas injection system 104 can introduce gases into the process chamber 102 for purging the process chamber 102, and for preparing, cleaning, and processing the substrates 110. The gas injection system 104 can, for example, include a liquid delivery system (LDS) (not shown) that contains a vaporizer to vaporize a silicon-containing liquid, e.g., hexachlorodisilane (Si_2Cl_6). The vaporized liquid can be flowed into the process chamber 102 with the aid of a carrier gas. Alternately, the gas injection system can include a bubbling system where a carrier gas is bubbled through a reservoir containing the silicon-containing liquid. In addition, the gas injection system 104 can be configured for flowing a gaseous silicon-containing gas, e.g., silane (SiH_4), from a high-pressure container. Furthermore, the above-mentioned gas flows can, for example, contain an inert gas. A plurality of gas supply lines can be arranged to flow gases into the process chamber 102. The gases can be introduced into volume 118, defined by the inner section 116, and exposed to substrates 110. Thereafter, the gases can flow into the volume 120, defined by the inner section 116 and the outer section 114, and exhausted from the process chamber 102 by the vacuum pumping system 106.

[0029] Substrates 110 can be loaded into the process chamber 102 and processed using substrate holder 112. The batch-type processing system 100 can allow for a large number of tightly stacked substrates 110 to be processed, thereby resulting in high substrate throughput. A substrate batch size can, for example, be about 100 substrates (wafers), or less. Alternately, the batch size can be about 25 substrates, or less. The process chamber 102 can, for example, process a substrate of any size, for example 200 mm substrates, 300 mm substrates, or even larger substrates. The substrates 110 can, for example, comprise semiconductor substrates (e.g. silicon or compound semiconductor), LCD substrates, and glass substrates.

[0030] The batch-type processing system 100 can be controlled by a controller 124 capable of generating control voltages sufficient to communicate and activate inputs of the batch-type processing system 100 as well as monitor outputs from the batch-type processing system 100. Moreover, the controller 124 can be coupled to and exchange information with process chamber 102, gas injection system 104, heater 122, process

monitoring system 108, and vacuum pumping system 106. For example, a program stored in the memory of the controller 124 can be utilized to control the aforementioned components of the batch-type processing system 100 according to a stored process recipe. One example of controller 124 is a DELL PRECISION WORKSTATION 610TM, available from Dell Corporation, Dallas, Texas.

[0031] Real-time process monitoring can be carried out using process monitoring system 108. In general, the process monitoring system 108 is a versatile monitoring system and can, for example, comprise a mass spectrometer (MS) or a Fourier Transform Infra-red (FTIR) spectrometer. The process monitoring system 108 can provide qualitative and quantitative analysis of the gaseous chemical species in the process environment. Process parameters that can be monitored include gas flows, gas pressure, ratios of gaseous species, and gas purities. These parameters can be correlated with prior process results and various physical properties of the deposited silicon-containing film.

[0032] FIG. 4 shows a simplified block diagram of another batch-type processing system for forming a SiGe surface layer on a substrate according to an embodiment of the invention. The batch-type processing system 1 contains a process chamber 10 and a process tube 25 that has an upper end connected to an exhaust pipe 80, and a lower end hermetically joined to a lid 27 of cylindrical manifold 2. The exhaust pipe 80 discharges gases from the process tube 25 to a vacuum pumping system 88 to maintain a pre-determined atmospheric or below atmospheric pressure in the processing system 1. A substrate holder 35 for holding a plurality of substrates (wafers) 40 in a tier-like manner (in respective horizontal planes at vertical intervals) is placed in the process tube 25. The substrate holder 35 resides on a turntable 26 that is mounted on a rotating shaft 21 penetrating the lid 27 and driven by a motor 28. The turntable 26 can be rotated during processing to improve overall film uniformity or, alternately, the turntable can be stationary during processing. The lid 27 is mounted on an elevator 22 for transferring the substrate holder 35 in and out of the reaction tube 25. When the lid 27 is positioned at its uppermost position, the lid 27 is adapted to close the open end of the manifold 2.

[0033] A plurality of gas supply lines can be arranged around the manifold 2 to supply a plurality of gases into the process tube 25 through the gas supply lines. In FIG. 4, only one gas supply line 45 among the plurality of gas supply lines is shown. The gas supply line 45 is connected to a gas injection system 94. A cylindrical heat reflector 30 is disposed so as to cover the reaction tube 25. The heat reflector 30 has a mirror-finished inner surface to suppress dissipation of radiation heat radiated by main heater 20, bottom heater 65, top heater 15, and exhaust pipe heater 70. A helical cooling water passage (not shown) is formed in the wall of the process chamber 10 as a cooling medium passage.

[0034] A vacuum pumping system 88 comprises a vacuum pump 86, a trap 84, and automatic pressure controller (APC) 82. The vacuum pump 86 can, for example, include a dry vacuum pump capable of a pumping speed up to 20,000 liters per second (and greater). During processing, gases can be introduced into the process chamber 10 via the gas injection system 94 and the process pressure can be adjusted by the APC 82. The trap 84 can collect unreacted precursor material and by-products from the process chamber 10.

[0035] The process monitoring system 92 comprises a sensor 75 capable of real-time process monitoring and can, for example, comprise a MS or a FTIR spectrometer. A controller 90 includes a microprocessor, a memory, and a digital I/O port capable of generating control voltages sufficient to communicate and activate inputs to the processing system 1 as well as monitor outputs from the processing system 1. Moreover, the controller 90 is coupled to and can exchange information with gas injection system 94, motor 28, process monitoring system 92, heaters 20, 15, 65, and 70, and vacuum pumping system 88. As with the controller 124 of FIG. 3, the controller 90 may be implemented as a DELL PRECISION WORKSTATION 610™.

[0036] FIG. 5 shows a simplified block diagram of a processing tool for forming a semiconductor device according to an embodiment of the invention. The processing tool 500 contains substrate loading chambers 510 and 520, processing systems 530–560, robotic transfer system 570, and controller 580. In one embodiment of the invention, formation of a SiGe surface layer, deposition of a high-k dielectric layer, performing an annealing process, and depositing an electrode layer, can be carried out in a single processing

system selected from systems 530-560. Alternately, these processes can be carried out in different processing systems. In one embodiment of the invention, formation of a SiGe surface layer can be carried out in processing system 540, deposition of a high-k dielectric layer and an annealing process can be carried out in processing system 550, and formation of an electrode layer can be carried out in processing system 560. In one embodiment of the invention, processing system 530 can be a plasma etch system for defining features in the semiconductor device. The use of multiple process chambers to form the semiconductor device be advantageous to reduce cross-contamination of different layers in the semiconductor device.

[0037] In another embodiment of the invention, the processing system 530 can be used as an analysis chamber for determining minimum dimensions of a semiconductor device. The process chamber 530 can, for example, be an Optical Digital Profilometer (ODP™) from TIMBRE Technologies, Santa Clara, CA.

[0038] The processing tool 500 can be controlled by a controller 580. The controller 580 can be coupled to and exchange information with substrate loading chambers 510 and 520, process chambers 530-560, and robotic transfer system 570. For example, a program stored in the memory of the controller 580 can be utilized to control the aforementioned components of the processing tool 500 according to a desired process, and to perform any functions associated with monitoring the process. One example of controller 570 is a DELL PRECISION WORKSTATION 610™, available from Dell Corporation, Dallas, Texas.

[0039] In one embodiment of the invention, at least one of the processing systems 530-560 can include a batch-type processing system or a single wafer processing system. In another embodiment of the invention, at least one of the processing systems 530-560 can include a thermal processing system, a plasma processing system, or an atomic layer deposition system.

[0040] Although only certain embodiments of this invention have been described in detail above, those skilled in the art will readily appreciate that many modifications are possible in the exemplary embodiment without materially departing from the novel teachings and advantages of this

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invention. Accordingly, all such modifications are intended to be included within the scope of this invention.